Hard Acid and Soft Nucleophile Systems. Part 13. Aluminum Chloride-Sodium Iodide-Acetonitrile System : A Very Mild Reagent for Selective Dealkylation (Commemoration Issue Dedicated to Professor Shigeo Tanimoto On the Occation of His Retirement)

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Hard Acid and Soft Nucleophile Systems. Part 13[1]. Aluminum Chloride —Sodium Iodide— Acetonitrile System :[2] A Very Mild Reagent for Selective Dealkylation

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A new combination reagent system ($AlCl_3$–NaI–CH_3CN) was devised for selective demethylation of aliphatic methyl ether in the presence of aromatic methyl ether under mild conditions. This reagent system cleaved the methyl ether of primary alcohol faster than that of secondary alcohol. The order of reactivity of ethers is aliphatic benzyl ether>aromatic benzyl ether, aliphatic methyl ether (primary>secondary)≫aromatic methyl ether. Benzyl ester and ethylene acetal were deprotected but methyl ester, acetate, lactone, and α,β-unsaturated ketone remained intact.

KEY WORDS: Aluminum chloride / Sodium iodide / Acetonitrile / Selective dealkylation / Methyl ether / Benzyl ether / Ethylene acetal / Benzyl ester / Hard acid / Soft nucleophile

The concept of "Hard" and "Soft" was introduced in chemistry in 1963 by Pearson and used to classify the various acids and bases[3]. The HSAB principle is an expression on reactivity that a hard acid combines with a hard base and a soft acid does with a soft base preferentially. Although the use of this principle had been limited only in inorganic chemistry in the early stage, this was also well recognized in the organic chemistry after the expansion into organic chemistry in 1967[4]. A chemical bond has the hard–soft dissymmetry as well as the charge dissymmetry. Thus, a combination system of a hard acid and a soft nucleophile may cleave the bond which consists of a hard base and a soft acid[5]. Previously we have developed various combination systems[6] of a hard Lewis acid and a thiol or a sulfide as a soft nucleophile for C–O bond cleavage reactions[7] of methyl ethers, benzyl ethers, esters, and lactones, according to the general concept as shown in Fig. 1.

To avoid foul smell of a thiol or a sulfide, we have devised a new combination system ($AlCl_3$–NaI–acetonitrile), where a thiol or a suifide is replaced by iodide ion

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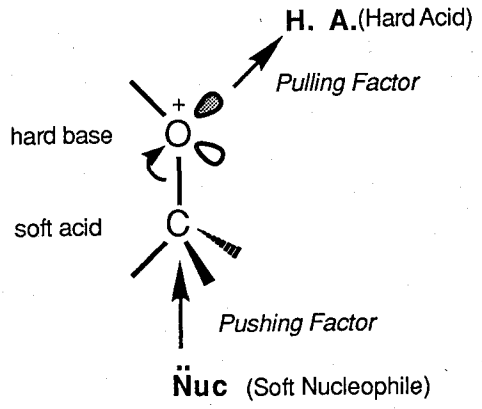


Fig. 1 Carbon-Oxygen Bond Cleavage Reaction

as a soft nucleophile. Here we will discuss the selectivities on dealkylation of methyl and benzyl ethers, and benzyl ester with $AlCl_3$–NaI–acetonitrile system.

Results and Discussion

Acetonitrile is a solvent of choice because it donates the electrons of the nitrogen to aluminum chloride to make a weak Lewis acid so that it dissolves aluminum chloride and also sodium iodide very well. Results of the demethylation of methyl ethers with this new combination system are listed in Table 1. Aliphatic primary and secondary methyl ethers **1a**–**6a** were easily cleaved by the present system at ambient temperature. The starting material **7a** was recovered in 98% yield at room temperature for 24 h. Refluxing temperature was required for demethylation of aromatic methyl ethers **7a** and **8a**. The observed difference in reactivity between aliphatic methyl ethers and aromatic methyl ethers indicates that the selective

Table 1 Demethylation of Methyl Ethers

Compound (mmol)	$AlCl_3$ (mmol)	NaI (mmol)	Cosolvent	Temp.	Time, h	Product (Yield, %)[a]
1a (0.2)	2.2	2.3	none	r. t.	8	**1b** (89)
2a (0.1)	1.0	1.1	CH_2Cl_2	r. t.	9	**2b** (90)
3a (0.026)	0.35	0.36	CH_2Cl_2	r. t.	20	**3b** (93)
4a (0.2)	2.0	2.0	CH_2Cl_2	r. t.	6	**4b** (91)
5a (0.2)	0.7	1.2	none	r. t.	5	**5b** (86)
6a (0.1)	1.0	1.0	none	r. t.	8	**6b** (95)
7a (0.2)	2.0	2.2	CH_2Cl_2	reflux	7	**7b** (92)
8a (0.2)	2.0	2.1	CH_2Cl_2	reflux	5	**8b** (86)
9a (0.1)	1.0	1.0	CH_2Cl_2	r. t.	5.5	**9b** (87)[b]
10a (0.25)	1.0	1.6	none	r. t.	5	**10b** (83)[c]
11a (0.6)	3.1	3.4	none	r. t.	5	**11b** (69) **11c** (27)

a) Isolated yield. b) An 8% yield of starting material was recovered. c) A 15% yield of diol was obtained.

demethylation of aliphatic methyl ether in the presence of aromatic methyl ether can be performed simply by controlling the reaction temperature. This idea was realized in selective demethylation of dimethyl ethers **9a** and **10a**. No report has been published on the selective demethylation of aliphatic methyl ether in the presence of the aromatic methyl ether in the same molecule, except for an example of estradiol dimethyl ether (**9a**) with a thiol–boron trifluoride etherate system[8]. Chemoselectivities observed with this reagent system were as follows. The acetate group in **3a** was not affected as the same with the aluminum chloride–thiol system[9]. Although the acetal group was deblocked to the corresponding carbonyl group, methyl ester and lactone ramained intact under the reaction conditions, as shown in the case of **6a**. The α, β–unsaturated ketone in **5a** survived under the reaction conditions, which were not tolarated on the aluminum chloride–thiol system[9]. It is worthy to point out the selective demethylation of the methyl ether of primary alcohol in the presence of that of the secondary alcohol in the case of **11a**. This differentiable ability of the new reagent system is very unique. There has been only one example of selective demethylation at a primary position in a permethylated thioglycoside reported by Hanessian[10].

The benzyl ethers and esters are commonly used as the protective group of alcohols and carboxylic acids[7]. These were also cleaved smoothly to give the parent alcohols, phenols or carboxylic acids in high yields as listed in Table 2. Generally, the debenzylation was proceeded more quickly than the demethylation. This is presumably due to the overlap of the p–orbital of benzene ring into the antibonding of $AlCl_3$–activated carbon–oxygen bond to facilitate the cleavage of C–O bond. This reagent system is especially useful for debenzylation of **5c**, for which the usual hydrogenolysis can not be used. The selective aliphatic benzyl ether cleavage was observed in the presence of the aromatic benzyl ether **9c**. The preferential debenzylation of benzyl ether of primary alcohol was performed cleanly in the presence of aromatic methyl ether in the case of **10c**. The selective benzyl ether deprotection of **12a** was proceeded to give **12b**. The same selective debenzylation on the ester **14a** was disclosed.

Table 2 Debenzylation of Benzyl Ethers or Benzyl Esters

Compound (mmol)	$AlCl_3$ (mmol)	NaI (mmol)	Temp.	Time, h	Product (yield, %)[a]
1c (0.2)	2.0	2.2	r. t.	1.5	**1b** (92)
4c (0.1)	1.0	1.1	r. t.	1.5	**4c** (86)
5c (0.1)	1.0	1.3	r. t.	1.0	**5c** (76)
9c (0.1)	1.0	1.0	0 ℃	2.0	**9d** (71)[b]
10c (0.13)	1.5	1.4	r. t.	1.3	**10b** (87)
12a (0.04)	0.44	0.44	0 ℃	3.5	**12b** (71)[c]
13a (0.33)	3.2	3.2	r. t.	3.0	**13b** (98)
14a (1.0)	10.4	10.8	r. t.	0.7	**14b** (86)
15a (0.43)	4.3	4.4	r. t.	4.0	**15b** (94)

a) Isolated yield. b) Estradiol (7%) and the starting material (21%) were obtained. c) Androsterone-3,17-diol (13%) and the starting material (16%) were obtained.

Ethylene acetal was deprotected as shown in **6a**, another ethylene acetal **16a**[11] also gave the parent carbonyl compound **16b** in 90% yield, in which naphthyl ester and naphthol remained intact.

The possible mechanism for this dealkylation is shown on demethylation in Chart 1. Lewis acidity of aluminum chloride is decreased to some extent by the coordination with acetonitrile to form a complex **A** (eq. 1). Addition of a methyl ether into the mixture attains the equilibrium (eq. 2), in which the bias depends upon the basicity of the oxygen atom. Because of the inductive effect of the phenyl ring and delocalization of the lone pair electrons on the oxygen over the aromatic ring, the basicity of the oxygen on the aromatic ring is somewhat decreased as compared to that of aliphatic ethers. As a result, the equilibrium shown in eq. 2 is

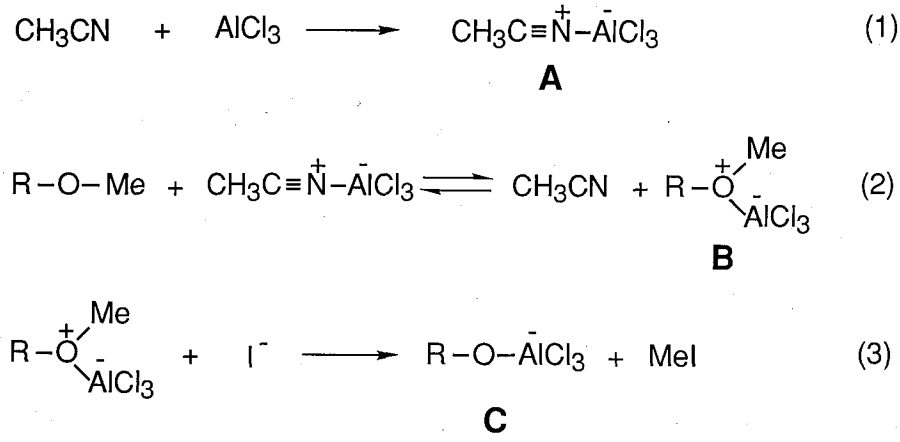
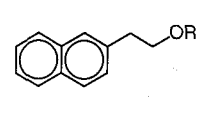
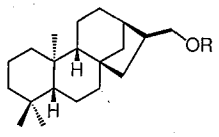


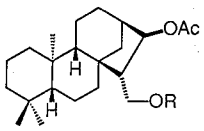
Chart 1



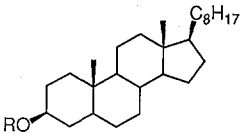
1a R = Me
1b R = H
1c R = Bn



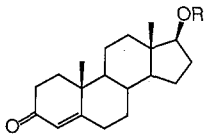
2a R = Me
2b R = H



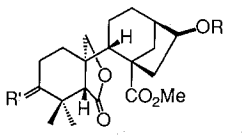
3a R = Me
3b R = H



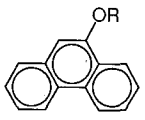
4a R = Me
4b R = H
4c R = Bn



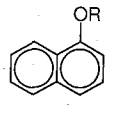
5a R = Me
5b R = H
5c R = Bn



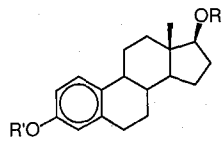
6a R = Me R' = O,O
6b R = H R' = O



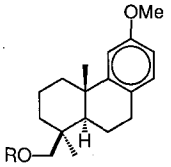
7a R = Me
7b R = H



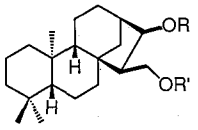
8a R = Me
8b R = H



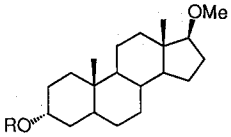
9a R = R' = Me
9b R = H, R' = Me
9c R = R' = Bn
9d R = H, R' = Bn



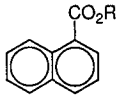
10a R = Me
10b R = H
10c R = Bn



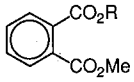
11a R = R' = Me
11b R = Me, R' = H
11c R = H, R' = Me



12a R = Bn
12b R = H



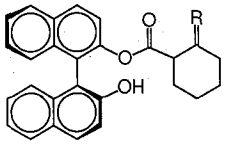
13a R = Bn
13b R = H



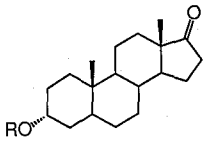
14a R = Bn
14b R = H

$CH_3(CH_2)_{10}CO_2R$

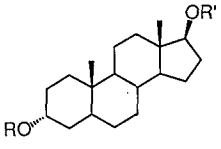
15a R = Bn
15b R = H



16a R = 
16b R = O



17 R = H
18 R = THP



19 R = THP, R' = H
20 R = THP, R' = Me

shifted to the right in aliphatic methyl ethers and to the left in aromatic methyl ethers. The oxonium ion **B** thus fromed is attacked by iodine ion at the less hindered methyl group followed by hydrolysis of the resulting **C** to comprete demethylation (eq. 3).

Conclusion

A key feature of *the hard acid and soft nucleophile system* involves an easy control of the dealkylating ability by the combination of a hard acid and a soft nucleophile as well as the using of dichloromethane as a co-solvent. Thus a balancing of the pulling factor and the pushing factor described in Fig. 1 makes it possible to dealkylate selectively. The pulling factor of hard acid is decreased in this new reagent system by the coordination with acetonitrile. This reagent system for dealkylation is characterized by followings. (1) The methyl ether of primary alcohol was demethylated preferentially to that of secondary alcohol. (2) Aliphatic methyl ether was exclusively deprotected in the presence of the aromatic methyl ether at room temperature. Refluxing condition was required for the demethylation of aromatic methyl ether. (3) Benzyl protective group of alcohols and carboxylic acids were selectively cleaved in the presence of the corresponding methyl protecting group. The order of reactivity of ethers is aliphatic benzyl ether>aromatic

benzyl ether, aliphatic methyl ether (primary>secondary)≫aromatic methyl ether. (4) Aliphatic methyl ether, benzyl ether, benzyl ester, and ethylene acetal were dealkylated, but methyl ester, acetate, lactone and α,β-unsaturated ketone remained intact. (5) Each component of the reagent system is inexpensive and readily available in laboratory and is easy to handle without any stench.

This new reagent system was already applied to the demethylation of methylated sugar in which the anchimeric effect was observed[12].

Acknowledgment

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Experimental

General Melting points were taken with a micro hot-stage apparatus (Yanagimoto) and were uncorrected. The infrared spectra were recorded with a JASCO A-202 diffraction grating infrared spectrophotometer and ^{1}H-NMR spectra were obtained with a JEOL JNM-FX-100 spectrometer or a Varian XL-300 or a JEOL JNM-GX-400 spectrometer in $CDCl_3$ with teramethylsilane as an internal standard. Mass spectra were determined on a JEOL JMS-DX 300 or a Hitachi M-80 mass spectrometer. Kieselgel 60 (70-230 mesh Merck) was used for column chromatography, and Kieselger 60 F-254 plates (Merck) for thin layer chromatography (TLC) and preparative TLC (PTLC).

Materials Methyl ethers **2a**[8], **3a**[13], **4a**[8], **6a**[14], **7a**[15], **9a**[8], **10a**[8], **11a**[13] and benzyl ethers **4c**[16], **5c**[17], **9c**[16], **14a**[18] were prepared according to the literatures. Methyl ether **8a** and benzyl ether **15a** are commercially available.

2-(2-Naphthyl)ethyl Methyl Ether (1a) To a solution of 2-(2-naphthyl) ethanol (861 mg, 5.0 mmol) in *N, N*-dimethylformamide (DMF) was added sodium hydride (60% in mineral oil) (456 mg, 11.4 mmol) at 0 ℃. After being stirred for 30 min methyl iodide (1.0 ml, 11.6 mmol) was added and stirred for 30 min at room temperature. The reaction mixture was poured into ice-water, acidified with dilute hydrochloric acid, extracted with ether, and followed by usual work-up. Purification by silica gel column chromatography gave **1a** (845 mg, 91%) as colorless oil: ^{1}H NMR δ 7.84-7.60 (m, 4 H, aromatic), 7.50-7.26 (m, 3 H, aromatic), 3.67 (t, J= 7 Hz, 2 H), 3.34 (s, 3 H), 3.03 (t, J= 7 Hz, 2 H); IR ($CHCl_3$) 1605, 1515 cm^{-1}; high-resolution MS calcd for $C_{13}H_{14}O$ (M^+) 186.108, found 186.106.

2-(2-Naphthy)ethyl Benzyl Ether (1c) To a solution of 2-(2-naphthyl) ethanol (344 mg, 2.0 mmol) in DMF was added sodium hydride (60 % in mineral oil) (400 mg, 10 mmol) at 0 ℃. After being stirred for 30 min, benzyl chloride (0.3 ml, 2.6 mmol) was added and stirred for 4 h at room temperature. The reaction mixture was poured into ice-water, acidified with dilute hydrochloric acid, extracted with ether and followed by usual work-up. Purification by silica gel column chromatography gave **1c** (476 mg, 91%) as colorless powder: mp 41.0-41.3 ℃ (MeOH); ^{1}H

NMR δ 7.84－7.60 (m, 4 H, aromatic), 7.48－7.32 (m, 3 H, aromatic), 7.25 (bs, 5 H), 4.52 (s, 2 H), 3.76 (t, J= 7 Hz, 2 H), 3.08 (t, J= 7 Hz, 2 H); IR ($CHCl_3$) 1602, 1360, 1095 cm^{-1}, MS 262 (M^+). Anal. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.91. Found: C, 87.09; H, 6.95.

Testosterone Methyl Ether (5a) To a solution of testosterone ethylene acetal (166 mg, 0.5 mmol) in DMF was added sodium hydride (60% in mineral oil) (275 mg, 6.9 mmol) at 0 ℃. After being stirred for 10 min methyl iodide (0.5 ml, 8.0 mmol) was added and stirred for 100 min at room temperature. The reaction mixture was poured into ice–water, acidified with dilute hydrochloric acid, extracted with ether and followed by usual work–up. To an acetone (20 ml) solution of this residue 5% hydrochloric acid (10 ml) was added and stirred for 13 h at room temperature. Extraction with dichloromethane and purification by silica gel column chromatography gave **5a** (133 mg, 88%) as coloress powder: mp 126.0－126.5 ℃ (MeOH); ^1H NMR δ 5.70 (bs, 1 H), 3.31 (s, 3 H), 3.22 (t, J= 8 Hz, 1 H), 1.18 (s, 3 H), 0.79 (s, 3 H); IR ($CHCl_3$) 1660, 1095 cm^{-1}; MS 302 (M^+). Anal Calcd for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00. Found; C, 79.22; H, 9.86.

Preparation of 10c To a solution of methyl *O*–methylpodocarpate (302 mg, 1.0 mmol) in ether was added lithium aluminum hydride (190 mg, 5.0 mmol) at 0 ℃ and stirred for 21 h at room temperature. The reaction mixture was poured into ice–water and acidified with dilute hydrochloric acid and extracted with ether then followed by the usual work–up. To a solution of the residue in DMF (10 ml) were added sodium hydride (60% in mineral oil) (470 mg, 11.8 mmol) and benzyl chloride (1.0 ml, 8.7 mmol) at 0 ℃. After being stirred for 20 h at room temperature, the reaction mixture was poured into ice–water and acidified with dilute hydrochloric acid and extracted with ether and worked up as usual. Purification by silica gel column chromatography gave **10c** (267 mg, 73%) as a colorless oil: ^1H NMR δ 7.36－7.12 (bs, 5 H, aromatic), 6.88 (d, J= 8 Hz, 1 H, aromatic), 6.74 (d, J= 3 Hz, 1 H, aromatic), 6.58 (dd, J= 8 and 3 Hz, 1 H, aromatic), 4.45 (s, 2 H), 3.69 (s, 3 H), 2.58 and 2.32 (ABq, J= 9 Hz, each 1 H), 1.12 (s, 3 H), 1.08 (s, 3 H); IR ($CHCl_3$) 1610, 1555 cm^{-1}; high–resolution MS calcd for $C_{25}H_{32}O_2$ (M^+) 364.240, found 364.237.

Preparation of 17 –Methoxyandrostanyl Benzyl Ether (12a)

To a solution of androsterone **17** (236 mg, 0.85 mmol) in dichloromethane (12 ml) were added dihydropyran (0.12 ml, 1.3 mmol) and pyridinium *p*–toluenesulfonate (PPTS) (44 mg, 0.17 mmol) at room temperature and stirred for 6 h. The reaction mixture was poured into ice–water and extracted with dichloromethane and followed by the usual work–up. Purification by silica gel column chromatogaphy gave tetrahydropyranyl androsterone **18** (288 mg, 92%).

To a solution of tetrahydropyranyl androsterone **18** (176 mg, 0.48 mmol) in methanol (5 ml) was added sodium borohydride at room temperature. After being stirred for 1.5 h, the reaction mixture was poured into ice–water and extracted with dichloromethane and followed by the usual work–up to give crude **19**.

To a solution of crude **19** in DMF (5 ml) were added sodium hydride (60% in mineral oil) (201 mg, 5.0 mmol) and methyl iodide (0.15 ml, 2.4 mmol) at 0 ℃. After being stirred for 3 h at room temperature, the reaction mixture was poured into ice–

water and extracted with ether and followed by the usual wolk-up to afford crude **20**. One drop of 10% hydrochloric acid was added to a solution of the obtained **20** in methanol (6 ml) then stirred for 2.5 h at room temperature. The reaction mixture was poured into ice-water and extracted with dichloromethane and worked up as usual. Purification by silica gel column chromatography gave **12b** (121 mg, 83%), which was recrystallized from dichloromethane-methanol to afford analytical sample: colorless powder; mp 169.0 - 169.5 ℃ (CH_2Cl_2-MeOH); ^{1}H NMR δ 4.02 (bs, 1 H), 3.32 (s, 3 H), 3.22 (t, J= 8 Hz, 1 H), 0.74 (s, 3 H), 0.78 (s, 3 H); MS 306 (M^+). Anal. Calcd for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18. Found; C, 78.10; H, 10.95.

To a solution of **12b** (110 mg, 0.36 mmol) in DMF (5ml) were added sodium hydride (60 % in mineral oil) (164 mg, 4.1 mmol) and benzyl chloride (0.2 ml, 1.7 mmol) at 0 ℃. After being stirred for overnight at room temperature, the reaction mixture was poured into ice-water and acidified with diluted hydrochloric acid, extracted with dichloromethane, worked up as usual. Purfication by silica gel column chromatogaphy gave **12a** (103 mg, 72%), which was recrystallized from ethyl acetate -methanol to afford colorless powder: mp 80.0 - 80.2 ℃ (AcOEt-MeOH); ^{1}H NMR δ 7.30 (s, 5 H), 4.44 (s, 2 H), 3.62 (bs, 1 H), 3.32 (s, 3 H), 3.20 (t, J= 8 Hz, 1 H), 0.78 (s, 3 H), 0.74 (s, 3 H); MS 396 (M^+). Anal. Calcd for $C_{27}H_{40}O_2$: C, 81.76; H, 10.17. Found; C, 82.08; H, 10.01.

Benzyl Naphthoate (13a) To a solution of naphthoic acid (1.72 g, 10.0 mmol) in benzene (30 ml) were added thionyl chloride (6 ml, 82 mmol) and several drops of DMF and stirred for 5 h at room temperature. After concentration of the solvent under the reduced pressure, dichloromethane (30 ml), benzyl alcohol (3 ml, 29 mmol) and triethylamine (3 ml, 22 mmol) were added to the obtained residue and stirred for 3 h. The reaction mixture was poured into ice-water and extracted with dichloromethane and worked up as usual. Purification by silica gel column chromatography gave **13a** (2.62 g, 100%) as colorless oil: ^{1}H NMR δ 8.90 (dd, J= 8 and 2 Hz, 1 H, aromatic), 8.20 - 7.20 (m, 11 H, aromatic), 5.36 (s, 2 H); IR ($CHCl_3$) 1705, 1515 cm^{-1}; high-resolution MS calcd for $C_{18}H_{14}O_2$ (M^+) 262.099, found 262.099.

General Procedure for Carbon-Oxygen Bond Cleavage Reaction with Aluminum Chloride-Sodium Iodide-Acetonitrile System

To a solution of a substrate (0.1 mmol) in acetonitrile (4 ml) and dichloromethane (2 ml) were added aluminum chloride and sodium iodide at 0 ℃ under nitrogen, the reaction mixture was stirred under the conditions described in Table 1 and 2. The reaction was followed by thin layer chromatography (TLC). The reaction mixture was poured into ice-water and extracted with dichloromethane. The organic layer was washed with aqueous sodium thiosulfate and brine, dried over sodium sulfate or magnesium sulfate, then concentrated *in vacuo*. Purification by silica gel column chromatography or preparative TLC gave the product which was identified with the authentic sample except for the case of unknown products.

Demethylation of 3a. To a solution of **3a** (9.5 mg, 0.026 mmol) in acetonitrile (0.5 ml) and dichloromethane (0.1 ml) were added aluminum chloride (46.2 mg, 0.35 mmol) and sodium iodide (54.6 mg, 0.36 mmol) at 0 ℃ then stirred for overnight at ambient temperature. According to the general procedure **3b** (8.5 mg, 94%) was ob-

tained as colorless powder: mp 190.0–190.2 ℃ (Et_2O); ^1H NMR δ 4.90 (dd, J= 6 and 4 Hz, 1 H), 3.72 (dd, A part of ABX, J= 11 and 5 Hz, 1 H), 3.46 (dd, B part of ABX, J= 11 and 9 Hz, 1 H), 2.38 (bs, 1 H), 2.07 (s, 3 H), 1.04 (s, 3 H), 0.85 (s, 3 H), 0.80 (s, 3 H); IR ($CHCl_3$) 3450, 1710, 1260 cm^{-1}; MS 348 (M^+). Anal. Calcd for $C_{22}H_{36}O_3$: C, 75.81; H, 10.41. Found; C, 75.66; H, 10.54.

Data for 6b: colorless powder; mp 229.8–230.3 ℃ (MeOH); ^1H NMR δ 4.44 and 4.04 (ABq, J= 10 Hz, each 1 H), 4.31 (m, 1 H), 3.65 (s, 3 H), 1.32 (s, 3 H), 1.21 (s, 3 H). IR ($CHCl_3$) 3620, 1770, 1715, 1240 cm^{-1}; high-resolution MS calcd for $C_{20}H_{28}O_6$ (M^+) 364.189, found 364.192.

Demethylation of 11a. To a solution of **11a** (197.1 mg, 0.59 mmol) in acetonitrile (4.0 ml) and dichloromethane (0.5 ml) were added aluminum chloride (410.5 mg, 3.08 mmol) and sodium iodide (513.6 mg, 3.42 mmol) at 0 ℃ than stirred for 2 h at ambient temperature. According to the general procedure **11b** (131.1 mg, 69%) and **11c** (50.8 mg, 27%) were obtained, which were recrystallized from methanol.

11b: colorless powder; mp 114.0–114.5 ℃ (MeOH); ^1H NMR δ 3.98 (dd, J= 12 and 6 Hz, 1 H), 3.87 (t, A part of ABX, 1 H), 3.59–3.30 (m, B part of ABX, 1 H), 3.34 (s, 3 H), 1.10 (s, 3 H), 0.84 (s, 3 H), 0.79 (s, 3 H); IR ($CHCl_3$) 3530, 1460, 1100 cm^{-1}; MS 320 (M^+). Anal. Calcd for $C_{21}H_{36}O_2$: C, 78.69; H, 11.32. Found; C, 78.65; H, 11.17.

11c: colorless powder; mp 84.5–85.5 ℃ (MeOH); ^1H-NMR δ 4.42 (dd, J= 10 and 7 Hz, 1 H), 3.70 (dd, A part of ABX, J= 12 and 8 Hz, 1 H), 3.42–3.28 (m, B part of ABX, 1 H), 3.36 (s, 3 H), 1.02 (s, 3 H), 0.84 (s, 3 H), 0.79 (s, 3 H); IR ($CHCl_3$) 3550, 1090 cm^{-1}; MS 320 (M^+). Anal. Calcd for $C_{21}H_{36}O_2$: C, 78.69; H, 11.32. Found; C, 78.81; H, 11.52.

(*S*)-2′-Hydroxyl-1,1′-binaphthalen-2-yl 2-cyclohexanonecarboxylate (16b)

A Mixture of (*S*)-2′-hydroxyl-1,1′-binaphthalen-2-yl 2,2-ethylenedioxycyclohexanecarboxylate **16a** (263 mg, 0.58 mmol), aluminum chloride (770 mg, 5.8 mmol), sodium iodide (869 mg, 5.8 mmol) in acetonitrile (6.0 ml) was stirred for 1.5 h. The reaction mixture was extracted with dichloromethane (50 ml, twice), and followed by the work-up described in the general procedure. (*S*)-2′-Hydroxyl-1,1′-binaphthalen-2-yl 2-cyclohexanonecarboxylate (**16b**) (213 mg, 90%) was obtained as a 1 : 1 mixture with its enol form: ^1H NMR δ 11.56 (s, 0.5 H, OH), 8.10–7.81 (m, 4 H), 7.55–7.45 (m, 2 H), 7.40–7.20 (m, 5 H), 7.08–7.01 (m, 1 H), 5.25 (brs, 0.5 H, OH), 5.20 (brs, 0.5 H, OH), 3.24–3.19 (m, 0.5 H), 2.26–2.12 (m, 2 H); MS (20 eV) 410 (M^+, 0.2), 287 (22), 286 (100), 257 (12), 239 (6), 115 (6); high-resolution MS calcd for $C_{27}H_{22}O_4$ (M^+) 410.152, found 410.152.

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